IGNITION AND COMBUSTION OF POWDERED METALS IN THE ATMOSPHERES OF VENUS, EARTH, AND MARS

R. A. Rhein, Senior Research Engineer

Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California, U.S.A.

ABSTRACT

The ignition temperatures of a number of powdered metals have been measured in air, in a simulated Venus atmosphere (consisting, by volume, of 4.10% argon, 9.17% nitrogen, and the remainder carbon dioxide) and in a simulated Mars atmosphere (consisting, by volume, of 2.16% argon, 11.21% carbon dioxide, and the remainder nitrogen). This study was conducted to show that the atmospheres of the planets Mars and Venus could be utilized as chemical energy sources.

Typical ignition temperatures of the following powdered metals were observed in the simulated Mars atmosphere: lithium, 405°C; beryllium, 762°C; calcium, 163°C; boron, 1203°C; cerium, 199°C; titanium, 916°C; zirconium, 614°C; thorium, 587°C; and uranium, 168°C. In the simulated Venus atmosphere, the following typical ignition temperatures were noted: lithium, 367°C; beryllium, earth ambient temperatures; magnesium, 676°C; calcium, 269°C; boron, 1000°C; aluminum, 705°C; cerium, 147°C; titanium, 708°C; zirconium, 152°C; thorium, 627°C; and uranium, 134°C. It was found that, generally, the powdered metals ignited more readily in air than in the Venus atmosphere, and more readily in the Venus atmosphere than in the Mars atmosphere.

This paper presents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by the National Aeronautics and Space Administration.

[redacted]

These ignition temperatures were compared to those in atmospheres of pure nitrogen and pure carbon dioxide. The performance of these propellants was discussed, and it was concluded that boron and beryllium are the preferred fuels.

1. Introduction

As part of a program to utilize the atmospheres of the planets as a source of chemical energy, various powdered metals were ignited in the simulated atmospheres of Mars and Venus, and, for comparison, ignited in air as well. The ignition temperatures were measured by placing a thermocouple, either chromel-alumel or platinum-platinum + 10% rhodium, into the mass of the powdered metal and impressing its output on a strip-chart recorder. The ignition temperature was easily seen as a discontinuous (i.e., very rapid) temperature increase as a function of time. In addition, the maximum combustion temperature was measured. The platinum-platinum +10% rhodium thermocouple was used when temperatures encountered were above the range of the chromel-alumel thermocouple.

The compositions, by volume, of the planetary atmospheres are currently considered to be: Venus, 5% argon, 10% nitrogen, and 85% carbon dioxide; Mars, 2% argon, 87% nitrogen, and 11% carbon dioxide. The gas mixtures used in these experiments were supplied by the Matheson Co., Inc., Antioch, Calif., with the following analyses: Venus atmosphere, 4.10% argon, 9.17% nitrogen, and the remainder carbon dioxide; Mars atmosphere, 2.16% argon, 11.21% carbon dioxide, and the remainder nitrogen.

This work is an extension of previous work (Ref. 1) which described the ignition and combustion, in nitrogen and in carbon dioxide, of the same powdered metals used here. The ignition temperature in air was found by placing a chromel-alumel thermocouple (0.010-in.-diameter wire) into the powdered metal, which filled a Coors crucible (size 000000). This crucible was set into a larger Coors crucible

[redacted]

(size 00), and was then heated by a torch. For studies in the Venusian and Martian atmospheres, the experiments were conducted in the apparatus shown in Fig. 1. The gas flow rate in each case was 100 ml/min. The apparatus shown in Fig. 1 was torch-heated very carefully in order to avoid hot spots. The heating was applied up to the ignition temperature and then removed. Several runs were made for each case of a particular powdered metal being heated in a particular atmosphere. Figures 2 and 3, which are representative, are displayed as thermocouple output vs time, and the ignition and maximum combustion temperatures are indicated. Figure 2 represents powdered calcium heated in a simulated Mars atmosphere; Fig. 3 represents powdered boron heated in a simulated Mars atmosphere. There was no attempt to vary the degree of metal subdivision here, but the ignition temperature may well vary with the degree of subdivision (Ref. 2).

2. Experimental Results

A. Lithium

Powdered lithium (less than 100-μ particle size, Lot No. 401-03, supplied by Foote Mineral Co., New Johnsonville, Tenn.) ignited in all three atmospheres. In each case, the lithium melted first, and the combustion appeared to be in the vapor phase. In the Venus atmosphere, the ignition temperatures were 367, 414, and 310°C.

In air, the combustion was irregular, with combustion intensity bursts superimposed on a steadily increasing combustion intensity. The ignition temperatures measured were 355 and 393°C.

In the simulated Mars atmosphere, the combustion definitely appeared to be in the vapor phase. The measured ignition temperatures were 433, 405, and 386°C.

B. Beryllium

The material used was a finely divided beryllium powder (less than 0.1-μ particle size, supplied by National Research Corp., Cambridge, Mass.). In all cases the combustion was very vigorous. The beryllium ignited in the Venus atmosphere, and also in air at room temperature.

In the Mars atmosphere, measured ignition temperatures were 553, 762, and 766°C. Once ignition occurred, the combustion was quite intense in all cases.

C. Magnesium

Magnesium powder (-325 mesh, rated 99.9% pure, supplied by Reade Mfg. Co., Inc., Los Angeles, Calif.) ignited in the Venus atmosphere at 641 and 676°C. The combustion was rather sluggish in both cases. In air, the ignition temperatures measured were 582 and 544°C. The combustion of magnesium powder in air was not very vigorous; rather it was quite sluggish. The magnesium powder did not ignite in the Mars atmosphere.

D. Calcium

Calcium powder (-325 mesh size, 99.9% pure, supplied by the Research Chemical Division of the Nuclear Corporation of America, Phoenix, Ariz.) ignited and burned vigorously in every case. In the Venus atmosphere, the ignition temperatures were 243 and 269°C. In air, the ignition temperatures were 222 and 236°C, followed by very vigorous combustion.

In the Mars atmosphere, the measured ignition temperatures were 192 and 163°C. The combustion was reasonably vigorous, but not so vigorous as in air or the Venus atmosphere.

E. Boron

Ultrafine boron powder (particle size less than 0.1-μ, 99% pure, Lot No. 2782-23-2, supplied by the Callery Chemical Company, Callery, Penn.) ignited in the Venus atmosphere at 858 and 1000°C. The combustion was reasonably vigorous.

In air, the measured ignition temperatures were 203 and 215°C. The combustion did not seem to be very vigorous.

In the Mars atmosphere, the measured ignition temperatures were 1172, 1203, and 1231°C.

F. Aluminum

Ultrafine aluminum powder (not oxide-stabilized, 0.02-μ particle size, Order No. BH5-2443-6, supplied by the National Research Corporation, Cambridge, Mass.) generally did not burn particularly vigorously, and did not burn in the Mars atmosphere at all. In one experiment in the Venus atmosphere, the ignition temperature was 705°C; the combustion was sluggish for a while, but terminated in a final flare-up. In another experiment, the ignition temperature was 671°C, but the combustion was never vigorous.

In air, the combustion was not at all vigorous. In one experiment, an ignition occurred at 466°C, and that combustion was rather sluggish. Heat was again applied, and another ignition occurred at 842°C. In another experiment, a weak ignition occurred at 610°C.

In the Mars atmosphere, no ignition occurred up to 1189°C.

G. Cerium

Cerium powder (-325 mesh size, Order No. BH4-288601, supplied by VARLACOID Chemical Company, New York, N.Y.) burned vigorously in every case. In the Venus atmosphere, ignition temperatures were recorded at 93, 147, and 212°C. In all cases, the combustion was very vigorous. In air, the ignition temperatures were measured at 115 and 108°C.

In the Mars atmosphere, the ignition temperatures were 197 and 199°C. The combustion was very vigorous.

H. Titanium

Powdered titanium (1-5-μ particle size, supplied by the A. D. Mackay Company, New York, N.Y.) ignited in all cases. In the Venus atmosphere, the ignition temperature was 708°C, and the combustion was vigorous and continued for about 1 min. It underwent a final burst, which terminated the combustion. Other experiments indicated ignition temperatures at 683 and 787°C.

In air, the ignition temperature was measured as 648 and 602°C. In the Mars atmosphere, the ignition temperature was measured at 830, 916, and 1007°C. The combustion was vigorous, albeit declining, and lasted perhaps 1 min, at which time the temperature dropped along a usual cooling curve as a function of time.

I. Zirconium

Zirconium powder (3-μ average particle size, 120-A grade, Lot No. 103-2, 94-95% pure, oxide impurity, Order No. BH4-288629, supplied by Charles Hardy, Inc., New York, N.Y.) ignited and burned vigorously in all cases, more so than did titanium. In the Venus atmosphere, the ignition temperatures were 156, 139, and 152°C. The combustion was very vigorous, and required perhaps 15 sec to reach its peak temperature.

In air, zirconium powder burned very intensely. The other experiments indicated that the ignition temperatures were 193, 197, and 240°C. In the Mars atmosphere, the experimental results indicated that the ignition temperatures were 578, 614, and 628°C.

J. Thorium

Powdered thorium (100% 200 mesh, 85% 325 mesh, Batch No. LW0521, supplied by the Rare Earth Division of the American Potash and Chemical Corporation, Los Angeles, Calif.) burned vigorously in every case. In the Venus atmosphere, the ignition temperatures were 627, 544, 552, and 685°C, and there was a fairly long combustion interval. The combustion was very intense; the ignition temperatures were 445 and 466°C.

In the Mars atmosphere, the combustion was rapid and intense. In the ignition experiments, the temperature was measured as 617, 574, and 587°C, with vigorous combustion in all three cases.

K. Uranium

Uranium-238 (depleted uranium, 200 mesh, coated with 2% viton, supplied by the Great Southern Manufacturing and Sales Company, Los Angeles, Calif.) burned in the various atmospheres, although sluggishly, presumably because of the viton coating. In the Venus atmosphere the ignition temperature was measured at 132 and 134°C; combustion was generally sluggish and irregular.

In air, the ignition temperatures were 157 and 133°C, and the combustion was reasonably intense. In the Mars atmosphere, ignition was strong, but combustion was sluggish. The ignition temperatures were 152 and 168°C.

3. Discussion

The present study of the ignition of powdered metals in mixtures of nitrogen and carbon dioxide, simulating the atmospheres of Mars and Venus, is compared in Table 1 with other studies of the ignition of the powdered metals in pure nitrogen and pure carbon dioxide.

Since the experimental conditions in the works by other authors are different from these employed by this writer in this work and in the study described in Ref. 1, some discrepancies in results may be expected.

This work indicated that ignition did occur with the powdered metals in the simulated planetary atmospheres, as well as their individual constituents. Although there was no attempt made here to delve into the theoretical or mechanistic aspects of metals burning, there are some excellent papers available (Ref. 2) regarding mechanistic studies of metals burning; one study, on the combustion of single aluminum particles (Ref. 10), presents an experimental approach to the understanding of metals combustion.

Since a number of the powdered metals did burn in the simulated atmosphere of Mars and Venus, they could be considered as chemical energy sources. The chemical energy obtainable per unit mass of metal, when burned in nitrogen and in carbon dioxide, is shown in Fig. 4. Included for comparison is the energy obtainable from the reaction of various fuel-oxidizer combinations per unit mass of a stoichiometric mixture of fuel and oxidizer. This data is tabulated in Fig. 4 under the heading "Inert Atmosphere". It is seen that boron or beryllium, burning in a nitrogen atmosphere, produces considerable heat, somewhat more so than the most space-storable fuel-oxidizer combinations, except for the systems $Li+OF_2$ and $Be+OF_2$. The boron produces somewhat more heat, in a nitrogen atmosphere, but the beryllium was more easily ignited. Weber and Mueller (Ref. 11) discussed ramjet and rocket applications of boron and beryllium in a nitrogen atmosphere. In a carbon dioxide atmosphere, Be, Li, B, and Al (and the boranes B_2H_6 and B_5H_9, which would probably burn in carbon dioxide) produce more energy per gram than any of the fuel-oxidizer combinations listed.

4. Conclusion

It is seen that there are a number of powdered metals which can burn in the simulated atmospheres of Venus and Mars. In many cases, the powdered metals burned about as readily in the simulated Venus atmosphere as in air, and most of the metal powders burned in the simulated Mars atmosphere. In order to take advantage of the atmosphere of Mars or Venus as a chemical energy source, more studies of powdered metal burning are required, and prototype burners must be developed.

REFERENCES

1. Rhein, R. A., The Ignition of Powdered Metals in Nitrogen and in Carbon Dioxide, Technical Report 32-679, Jet Propulsion Laboratory, Pasadena, California, December 1964.
2. M. Summerfield, Solid Propellant Rocket Research, Part C, "Combustion of Metals," Progress in Astronautics and Rocketry, Vol. 1, Academic Press, New York, New York, 1960, pp. 253-291.
3. Brown, H. R., Hartmann, Irving, and Nagy, John, Inflammability and Explosibility of Metal Powders, Investigation No. 3722, U.S. Bureau of Mines, Pittsburgh, Pennsylvania, 1943.
4. Dafert, F. W., and Mixlaue, R., "New compounds of nitrogen and hydrogen with the alkaline earth metals," Monatshefte Fūr Chemie Und Verwandte Teile Anderer Wissenschaften, Vol. 34, 1913, p. 1685.
5. Rhein, R. A., Unreported Research, Jet Propulsion Laboratory, Pasadena, California.
6. Wolf, J., "Synthesis of aluminum nitride from the elements," Zeitschrift Fūr Anorgamsche Und Allgemeine Chemie, Vol. 83, 1913, pp. 159-162.
7. Muthmann, W., and Kraft, K., "Investigations of cerium and lanthanium," Liebig's Annual, Vol. 325, 1902, pp. 261-278.
8. Hartmann, I., Jacobsen, M., and Nagy, J., Explosive Characteristics of Ti, Zr, Th, U, and Their Hydrides, Investigation No. 4835, U.S. Bureau of Mines, Pittsburgh, Pennsylvania, 1951.
9. Weiss, L., and Kaiser, H., "On metallic titanium," Zeitschrift Fūr Andrganische Und Allgemeine Chemie, Vol. 64, 1910, p. 352.
10. Friedman, R., and Macek, A., "Combustion studies of single aluminum particles," Ninth Symposium on Combustion, Academic Press, New York, 1963, pp. 703-712.

REFERENCES (Cont'd)

11. Mueller, K. H., and Weber, J. Q., "Theoretical performance of metals burning nitrogen for propulsion in the Martian atmosphere," Chemical Engineering Techniques in Aerospace, Chemical Engineering Progress, Vol. 60, Symposium Series, No. 52, New York, American Institute of Chemical Engineers, 1964, pp. 17-22.

FIGURE CAPTIONS

1. Ignition apparatus
2. Ultrafine beryllium heated in a simulated Venus atmosphere
3. Ultrafine boron heated in a simulated Mars atmosphere
4. Energy obtainable from the combustion of powdered metals in nitrogen and in carbon dioxide, per unit mass of metal, and energy obtainable from the reaction of various fuel/oxidizer combinations, per unit mass of stoichiometric mixture, in an inert atmosphere

Table 1. Ignition Tempera
M

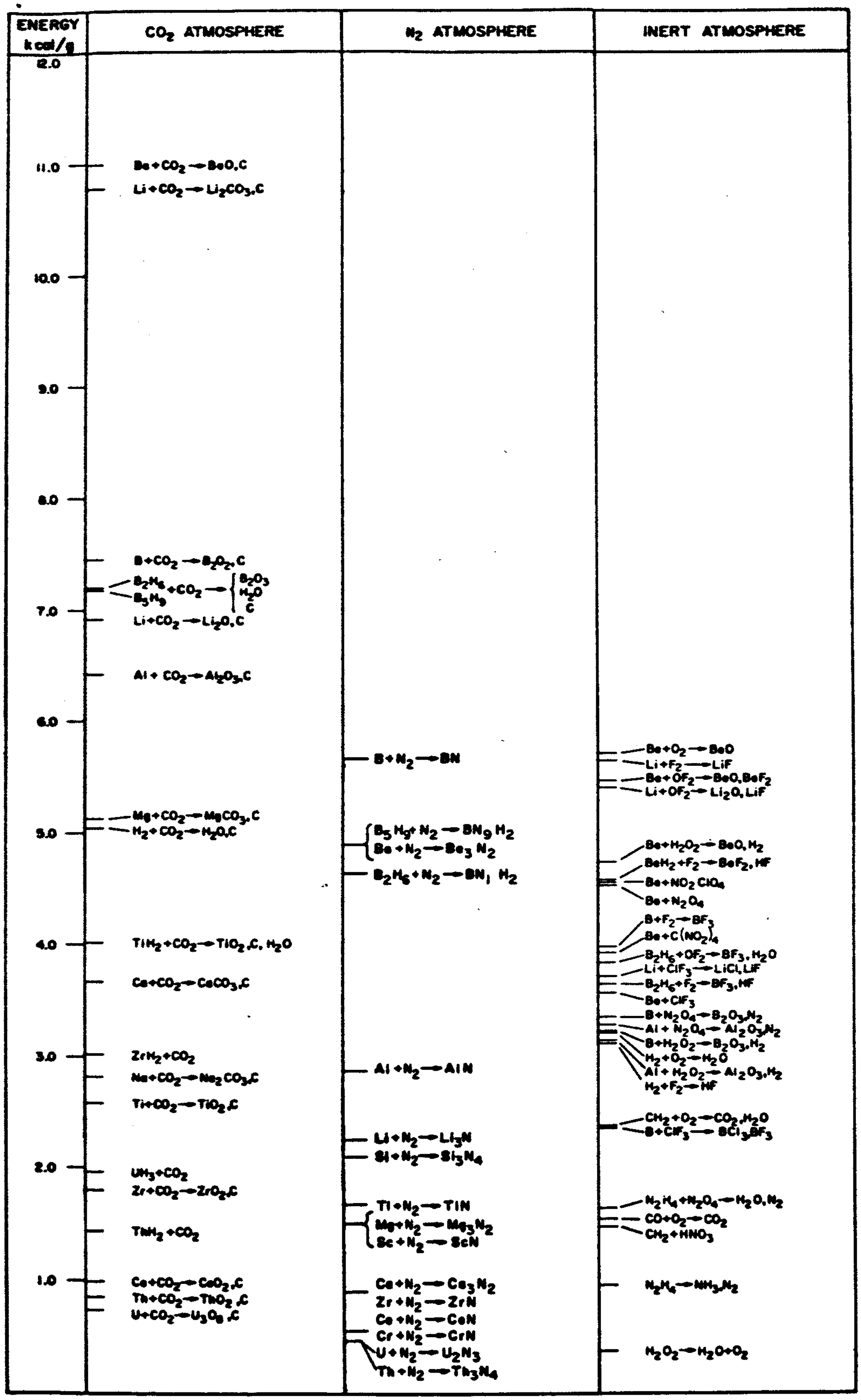
Metal	State or condition	N_2
Li	<100 µ	388,410
	<100 µ	
Be	<0.1 µ	504,527
	<0.1 µ	
Mg	-325 mesh	No ignition to 1071
	-325 mesh	
	100%/100 mesh, 86%/270 mesh	530
Ca	-325 mesh	327,360
	Finely divided	600
B	<0.1 µ	
	<0.1 µ	1059, 1440
Al	<0.1 µ	No ignition to 1080
	<0.1 µ	
	100%/100 mesh, 92%/270 mesh	
	Finely divided	820
Ce	-325 mesh	
	-325 mesh	216,230
	Fine wire	850
Ti	1-5 µ	
	99%/100 mesh, 62%/270 mesh	830
	10.5 µ	760
	Finely divided	800
Zr	3 µ	
	3 µ	490,525
	3.3 µ	790
	-325 mesh	530
Th	85%/1325 mesh, 100%/-200 mesh	
	-325 mesh	630
	7.2 µ	500
U	-200 mesh, viton coated	354,360
	-200 mesh, viton coated	
	10.8 µ	410

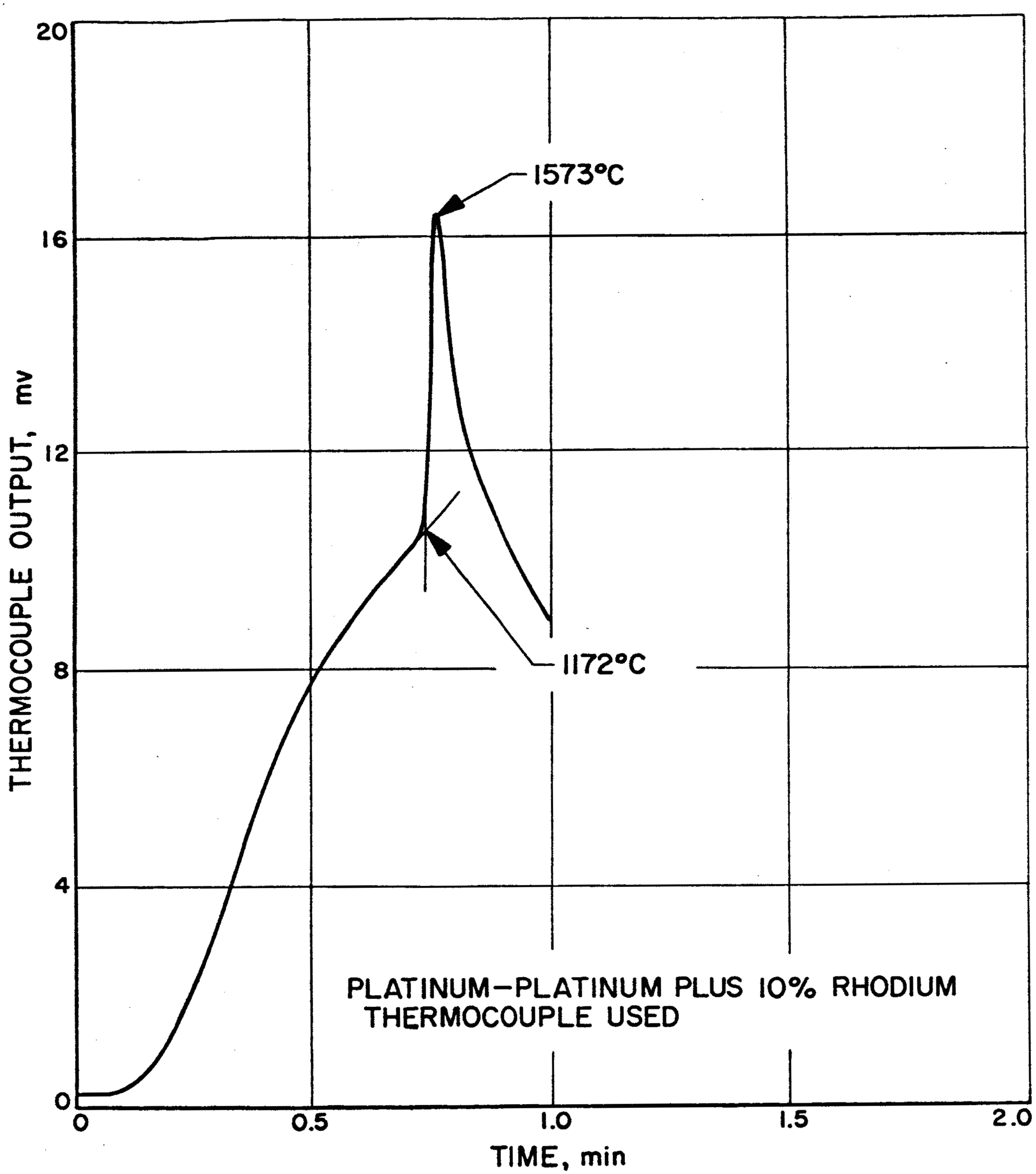
*This study

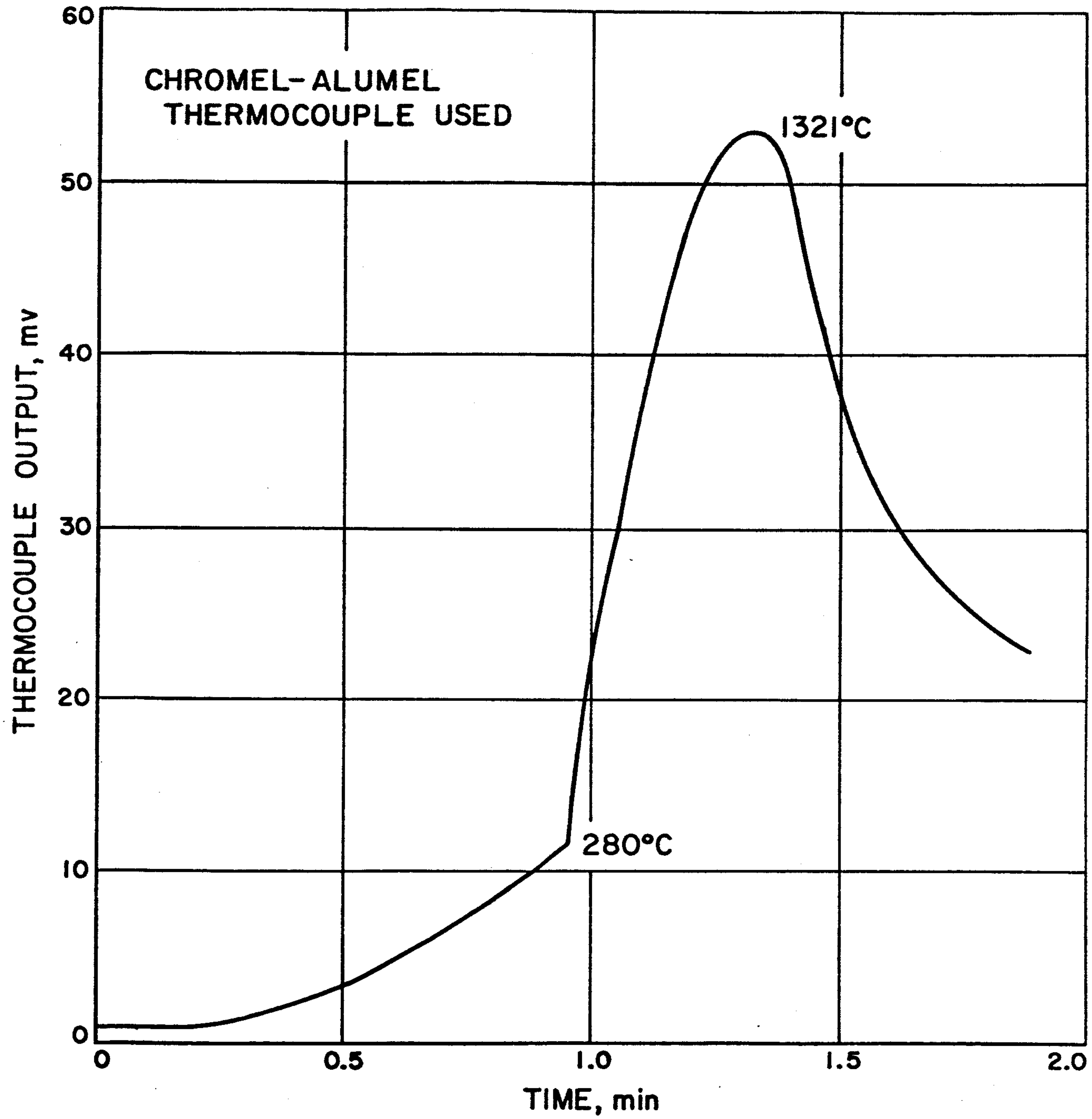
of Powdered Metals in Nitrogen, Simulated Atmospheres of
nd Venus, Carbon Dioxide, and Air

Ignition temperatures, °C		
Mars atmosphere 86.63% N_2 11.21% CO_2 2.16% Ar	Venus atmosphere 9.17% N_2 83.73% CO_2 4.10% AR	CO_2
433,405,386	367,414,310	330
553,762,766	Ambient	Ambient
No ignition	641,676	749 630
192,163	243,269	293
1172,1203,1231	858,1000	871,922,101
No ignition to 1180	671,705	360,420 655
197,199	93,147,212	172,190
830,916,1007	603,708,787	670,680 550
578,614,628	139,152,156	363,366 620 560
574,587,617	544,552,627,685	730 450
152,168	132,134	235 350

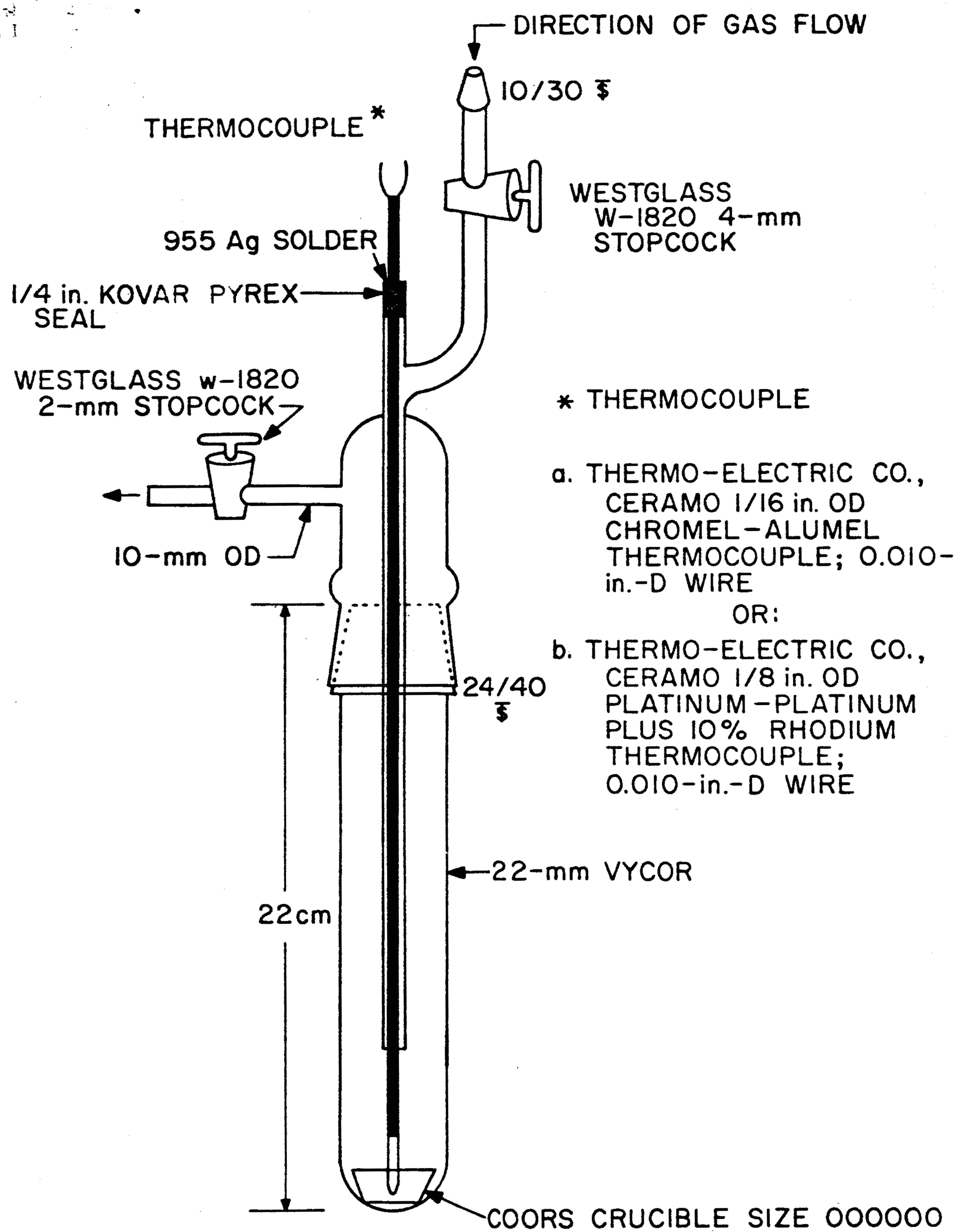
	Air	Ref.
		1
	353,393	*
		1
	Ambient	*
		1
	582,544	*
	490	2
	222,236	1
		*
	203,215	3
7		4
		1
	466,410	*
	585	2
		5
	115,108	*
		1
		6
	648,602	*
	460	1
		2
	510	7
		8
	193,197,240	*
		1
	190	7
	210	7
	445,466	*
		1
	280	7
		1
	133,157	*
	100	7


ENERGY k cal/g
CO_2 ATMOSPHERE
N_2 ATMOSPHERE
INERT ATMOSPHERE
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
$Be + CO_2 \rightarrow BeO, C$
$Li + CO_2 \rightarrow Li_2CO_3, C$
$B + CO_2 \rightarrow B_2O_2, C$
B_2H_6, B_5H_9 $+ CO_2 \rightarrow$ B_2O_3, H_2O, C
$Li + CO_2 \rightarrow Li_2O, C$
$Al + CO_2 \rightarrow Al_2O_3, C$
$Mg + CO_2 \rightarrow MgCO_3, C$
$H_2 + CO_2 \rightarrow H_2O, C$
$TiH_2 + CO_2 \rightarrow TiO_2, C, H_2O$
$Ca + CO_2 \rightarrow CaCO_3, C$
$ZrH_2 + CO_2$
$Na + CO_2 \rightarrow Na_2CO_3, C$
$Ti + CO_2 \rightarrow TiO_2, C$
$UH_3 + CO_2$
$Zr + CO_2 \rightarrow ZrO_2, C$
$ThH_2 + CO_2$
$Ce + CO_2 \rightarrow CeO_2, C$
$Th + CO_2 \rightarrow ThO_2, C$
$U + CO_2 \rightarrow U_3O_8, C$
$B + N_2 \rightarrow BN$
$B_5H_9 + N_2 \rightarrow BN_9 H_2$
$Be + N_2 \rightarrow Be_3N_2$
$B_2H_6 + N_2 \rightarrow BN, H_2$
$Al + N_2 \rightarrow AlN$
$Li + N_2 \rightarrow Li_3N$
$Si + N_2 \rightarrow Si_3N_4$
$Ti + N_2 \rightarrow TiN$
$Mg + N_2 \rightarrow Mg_3N_2$
$Sc + N_2 \rightarrow ScN$
$Ca + N_2 \rightarrow Ca_3N_2$
$Zr + N_2 \rightarrow ZrN$
$Ce + N_2 \rightarrow CeN$
$Cr + N_2 \rightarrow CrN$
$U + N_2 \rightarrow U_2N_3$
$Th + N_2 \rightarrow Th_3N_4$
$Be + O_2 \rightarrow BeO$
$Li + F_2 \rightarrow LiF$
$Be + OF_2 \rightarrow BeO, BeF_2$
$Li + OF_2 \rightarrow Li_2O, LiF$
$Be + H_2O_2 \rightarrow BeO, H_2$
$BeH_2 + F_2 \rightarrow BeF_2, HF$
$Be + NO_2ClO_4$
$Be + N_2O_4$
$B + F_2 \rightarrow BF_3$
$Be + C(NO_2)_4$
$B_2H_6 + OF_2 \rightarrow BF_3, H_2O$
$Li + ClF_3 \rightarrow LiCl, LiF$
$B_2H_6 + F_2 \rightarrow BF_3, HF$
$Be + ClF_3$
$B + N_2O_4 \rightarrow B_2O_3, N_2$
$Al + N_2O_4 \rightarrow Al_2O_3, N_2$
$B + H_2O_2 \rightarrow B_2O_3, H_2$
$H_2 + O_2 \rightarrow H_2O$
$Al + H_2O_2 \rightarrow Al_2O_3, H_2$
$H_2 + F_2 \rightarrow HF$
$CH_2 + O_2 \rightarrow CO_2, H_2O$
$B + ClF_3 \rightarrow BCl_3, BF_3$
$N_2H_4 + N_2O_4 \rightarrow H_2O, N_2$
$CO + O_2 \rightarrow CO_2$
$CH_2 + HNO_3$
$N_2H_4 \rightarrow NH_3, N_2$
$H_2O_2 \rightarrow H_2O + O_2$


1573°C
1172°C
PLATINUM–PLATINUM PLUS 10% RHODIUM
THERMOCOUPLE USED
THERMOCOUPLE OUTPUT, mv
20
16
12
8
4
0
0
0.5
1.0
1.5
2.0
TIME, min



CHROMEL-ALUMEL
THERMOCOUPLE USED
1321°C
280°C
THERMOCOUPLE OUTPUT, mv
0
10
20
30
40
50
60
0
0.5
1.0
1.5
2.0
TIME, min


DIRECTION OF GAS FLOW
10/30 $
THERMOCOUPLE *
WESTGLASS W-1820 4-mm STOPCOCK
955 Ag SOLDER
1/4 in. KOVAR PYREX SEAL
WESTGLASS w-1820 2-mm STOPCOCK
10-mm OD
* THERMOCOUPLE
a. THERMO-ELECTRIC CO., CERAMO 1/16 in. OD CHROMEL-ALUMEL THERMOCOUPLE; 0.010-in.-D WIRE
OR:
b. THERMO-ELECTRIC CO., CERAMO 1/8 in. OD PLATINUM-PLATINUM PLUS 10% RHODIUM THERMOCOUPLE; 0.010-in.-D WIRE
24/40 $
22-mm VYCOR
22cm
COORS CRUCIBLE SIZE 000000